Entropy and Solubility: Why Don’t Oil and Water Mix?\textsuperscript{113}

The fact that oil and water do not mix is well known. It has even become a common metaphor for other things that do not mix (people, faiths, etc.) What is not quite so well known is, why? Oil is a generic name for a group of compounds, many of which are hydrocarbons or contain hydrocarbon-like regions. Oils are – well – oily, they are slippery and (at the risk of sounding tedious) unable to mix with water. The molecules in olive oil or corn oil typically have a long hydrocarbon chain of about 16–18 carbons. These molecules often have polar groups called esters (groups of atoms that contain C—O bonds) at one end.\textsuperscript{114} Once you get more than six carbons in the chain, these groups do not greatly influence solubility in water, just as the single O —H groups in most alcohols do not greatly influence solubility. So, oily molecules are primarily non-polar and interact with one another as well as with other molecules (including water molecules), primarily through London dispersion forces (LDFs). When oil molecules are dispersed in water, their interactions with water molecules include both LDFs and interactions between the water dipole and an induced dipole on the oil molecules. Such dipole–induced dipole interactions are common and can be significant. If we were to estimate the enthalpy change associated with dispersing oily molecules in water, we would discover ΔH is approximately zero for many systems. This means that the energy required to separate the molecules in the solvent and solute is about equal to the energy released when the new solvent–solute interactions are formed.

Remember that the entropy change associated with simply mixing molecules is positive. So, if the enthalpy change associated with mixing oils and water is approximately zero, and the entropy of mixing is usually positive, why then do oil and water not mix? It appears that the only possibility left is that the change in entropy associated with dissolving oil molecules in water must be negative (thus making ΔG positive.) Moreover, if we disperse oil molecules throughout an aqueous solution, the mixed system spontaneously separates (unmixes). This seems to be a process that involves work. What force drives this work?

Rest assured, there is a non-mystical explanation but it requires thinking at both the molecular and the systems level. When hydrocarbon molecules are dispersed in water, the water molecules rearrange to maximize the number of H-bonds they make with one another. They form a cage-like structure around each hydrocarbon molecule. This cage of water molecules around each hydrocarbon molecule is a more ordered arrangement than that found in pure water, particularly when we count up and add together all of the individual cages! It is rather like the arrangement of water molecules in ice, although restricted to regions around the hydrocarbon molecule. This more ordered arrangement results in a decrease in entropy. The more oil molecules disperse in the water, the larger the decrease in entropy. On the other hand, when the oil molecules clump together, the area of “ordered water” is reduced; fewer water molecules are affected. Therefore, there is an increase in entropy associated with the clumping of oil molecules—a totally counterintuitive idea! This increase in entropy leads to a negative value for –TΔS, because of the negative sign. Therefore, in the absence of any other factor the system moves to minimize the interactions between oil and water molecules, which leads to the formation of separate oil and water phases. Depending on the relative densities of the substances, the oily phase can be either above or below the water phase. This entropy-driven separation of oil and water molecules is commonly referred to as the hydrophobic effect. Of course, oil molecules are not afraid (phobic) of water, and they do not repel water molecules. Recall that all molecules will attract each other via London dispersion forces (unless they have a permanent and similar electrical charge).

The insolubility of oil in water is controlled primarily by changes in entropy, so it is directly influenced by the temperature of the system. At low temperatures, it is possible to stabilize mixtures of water and hydrocarbons. In such mixtures, which are known as clathrates, the hydrocarbon molecules are surrounded by stable cages of water molecules (ice). Recall that ice has relatively large open spaces within its crystal structure. The hydrocarbon molecules fit within these holes, making it possible to predict the maximum size of the hydrocarbon molecules that can form clathrates. For example,
some oceanic bacteria generate CH4 (methane), which is then dissolved in the cold water to form methane clathrates. Scientists estimate that between two and ten times the current amount of conventional natural gas resources are present as methane clathrates.115

References


114 See additional materials for structures and names of functional groups.

115 http://en.wikipedia.org/wiki/Methane_clathrate